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Supporting Information

Host–Guest Complexation of Amphiphilic Molecules at the Air–Water Interface Prevents Oxidation by Hydroxyl Radicals and Singlet Oxygen

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Materials and methods

The guanidinium-modified calix[5]arene pentadodecyl ether[1] (G·5HCl) and 4-(dodecyloxy)benzamido-terminated methoxy poly(ethyleneglycol)[2] (PEG-C12) were synthesized and purified according to our previous procedures. Oleic acid (OA) was purchased from Avanti Polar Lipids (Alabaster, AL) and used without further purification. Temoporfin (T) was purchased from Sigma Aldrich (St. Louis, MO) and used without further purification. All solvents (water and methanol) are HPLC grade and purchased from EMD Chemicals Inc. (Gibbstown, NJ, USA). 2 mM stock solutions of these molecules are firstly obtained by dissolving the chemicals in methanol, and then diluted by water to make solutions of 50 μM pure OA, 50 μM OA/50 μM G·5HCl mixture, and 50 μM OA/50 μM G·5HCl/25 μM T mixture.

The HEPES buffer solution of pH 7.4 was prepared by dissolving 2.38 g of 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (HEPES) in approximate 900 mL double-distilled water. Then, the solution was titrated to pH 7.4 at the 25 °C with NaOH. The pH value of the buffer solution was measured on a pH-meter calibrated with three standard buffer solutions. Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a Cary Eclipse equipped with a Cary single-cell peltier accessory. Fluorescein (Fl) was purchased from Tokyo Chemical Industry and used without further purification. G·5HCl and PEG-C12 (molar ratio 2:1) were dissolved in a mixture solution of methanol and chloroform (2:1, v/v). PEG-C12 doping is for enhancing water-solubility of G·5HCl to hydrate in mild conditions.[2] After removal of solvent under reduced pressure for 12 h, the residue was hydrated in HEPES buffer (10 mM, pH = 7.4) by sonication at 80 °C for 3−5 h to obtain the 100 μM G nanoparticle stock solution. Both stock solutions (100 μM) of Fl and OA were obtained by dissolving the chemicals in HEPES buffer. Diluting stock solutions made a solution of 1.0 μM G·5HCl/0.5 μM Fl nanoparticle mixture for titration in a quartz cell. The competitive fluorescence titrations were performed by successive addition of known amounts of OA (up to 4.03 μM) to the solution in cell. The data were well fitted by a 1:1 competitive binding model.

Figure S1 presents the schematic drawing of the FIDI-MS setup. Briefly, a hanging droplet of ~2 mm o.d. (~4 μL in volume) is suspended on the end of a stainless steel capillary between two parallel plate electrodes separated by 6.3 mm. Droplets are formed from liquid fed through the capillary using a motorized syringe pump. The parallel plates are mounted on a translation stage to allow alignment of an aperture in the electrically grounded plate with the atmospheric pressure inlet of an LTQ-XL mass spectrometer (Thermo-Fisher, Waltham, MA). The capillary is mounted on a separate translation stage to place the droplet exactly midway between the two plates and to align with the inlet of the LTQ-XL. Mass spectrometric sampling of the hanging droplet is accomplished by applying a pulsed high voltage (typically 3 to 5 kV, 5 ms duration, polarity selected to sample either positive or negative ions) to the

back parallel plate and to the capillary at half the magnitude applied to the back plate to maintain field homogeneity between the front and back plate. When a sufficiently high voltage is applied, bipolar ejection of highly-charged progeny droplets less than 1 μm in diameter from the opposite ends of the suspended droplet ensues. Charged droplets of a selected polarity enter the transfer capillary of the mass spectrometer, resulting in the detection of gas-phase ions. In this study, we apply positive voltage on the back plate in order to detect protonated G, G·OA complexes, T, and their oxidation products, and negative voltage to detect deprotonated OA and its oxidation products. When each droplet is initially formed, we allow 60 seconds for the molecules to diffuse to the air-water interface before exposing the droplet to hydroxyl radicals or the red light (650 nm) emitted from a laser pointer for a variable reaction time. After the reactions, we trigger the high voltage to sample both reactants and products. Sampling occurs on a millisecond time scale. Each experiment starts with a fresh drop.

OH is generated using a dielectric barrier discharge source (DBDS) composed of a borosilicate tube (1/4" OD, 3/16" ID) which acts as the dielectric material. A tungsten filament inner electrode is sealed within the tube, and a conductive silver epoxy coating (McMaster-Carr, Santa Fe Springs, CA, USA) acts as an outer electrode. A glass bubbler provides water saturated helium through the DBDS, with a flow of 1000 mL/min monitored by a Type πMFC Digital Mass Flow Controller (Model PFC-50, MKS Instruments). A high voltage AC power supply (Trek PM04015) biased the inner electrode during experiments at 12 kV (peak to peak) and 1000 Hz, while the outer electrode remained grounded. Between the power supply and the tungsten filament, there is a 1 MΩ resistor as the current limiter. A low temperature plasma (dielectric barrier discharge) is generated inside the tube, producing hydroxyl radicals in the gas flow. Compared to the tropospheric OH radical concentration that was measured to be 1-3 × 10^6 molecules/cm^3,[3] the DBDS can generate ~1×10^9 molecules/cm^3 OH radicals[4] based on the time required to oxidize a monolayer of surfactant with an average of one oxygen per surfactant molecule. The high concentration of OH radicals significantly accelerates the oxidation process compared to ambient conditions.

SDO is generated by illuminating the hanging droplet containing the photosensitizer T with a 650 nm laser pointer (0.345 mW/cm^2, Figure S2), close to its activation wavelength, 652 nm.[5]

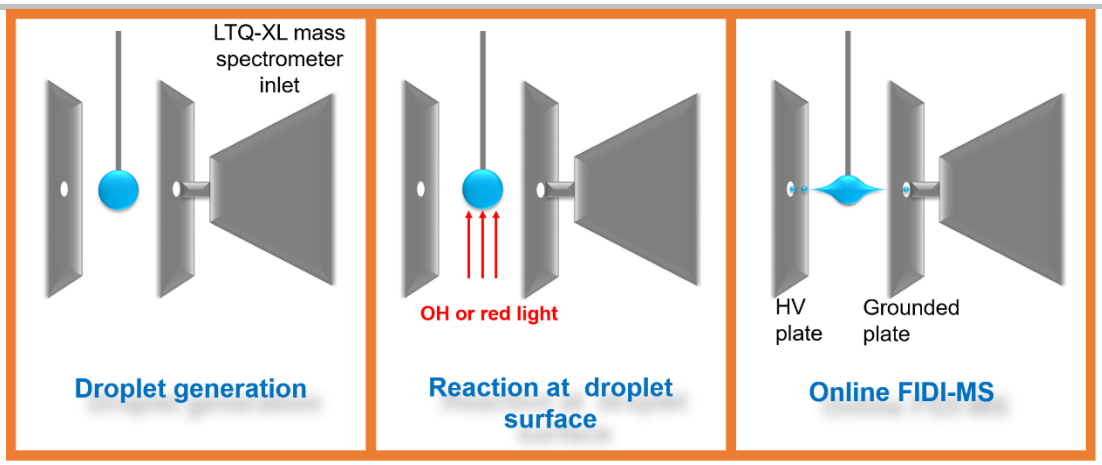

Figure S1. Schematics of the FIDI-MS setup.

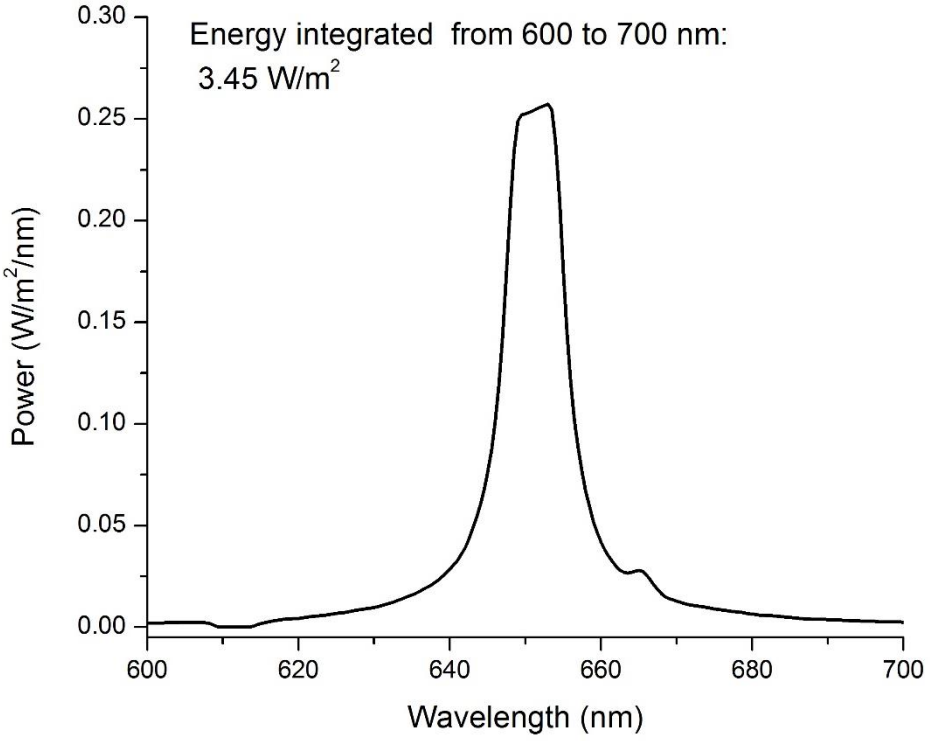

Figure S2. The output of the laser pointer measured in the current experiment by a Black-Comet UV-VIS spectrometer (StellarNet, Inc.). The energy integrated from 600 to 700 nm is 0.345 mW/cm^2, making the energy delivered to a 2 mm diameter droplet 0.01 mW.

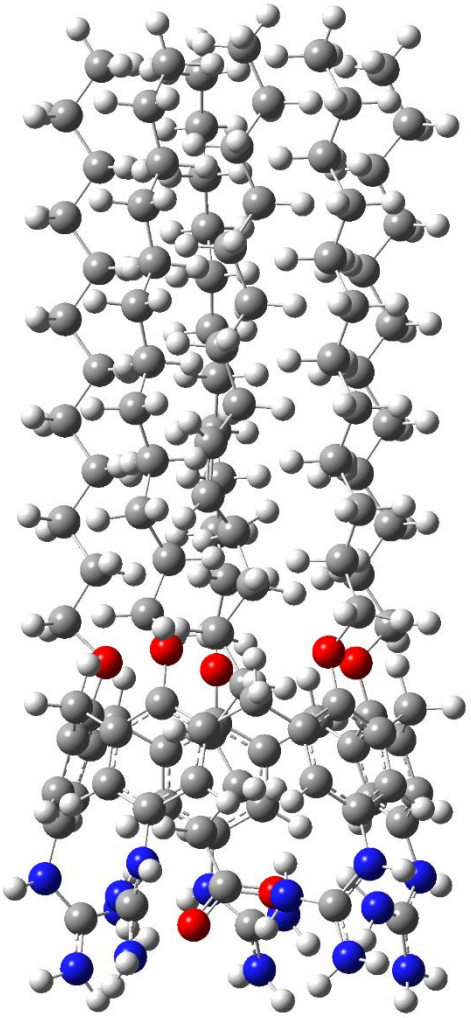

Figure S3. Density functional theory (DFT) calculation of the G·OA complex at the B3LYP/6-31G(d) level of theory. The heights of G and OA are almost the same (oxygen, red sphere; carbon, gray sphere; nitrogen, blue sphere; hydrogen, white sphere).

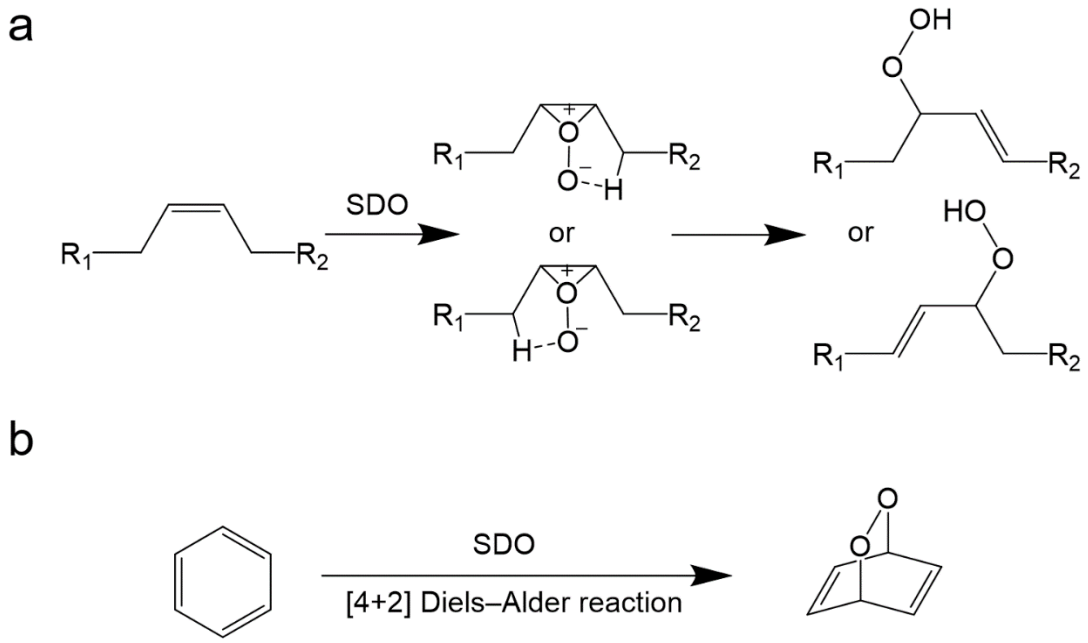

Figure S4. Reaction mechanisms of SDO. The C=C double bond in **a** belongs to OA, and the benzene moiety in **b** belongs to G.

References

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